

PROCESS FOR THE TREATMENT OF WASTE GAS AND UNIT SUITABLE  
FOR USE THEREIN

CROSS REFERENCE TO RELATED APPLICATION

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Priority of this application is based on European Patent Application No. 02079960.7, filed November 27, 2002, and U.S. Provisional Application No. 60/432,287, filed December 10, 2002, both of which are herein incorporated by reference.

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BACKGROUND OF THE INVENTION

Field of the Invention

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The present invention pertains to a process for the treatment of waste gas. It also pertains to a unit suitable for use therein.

Prior Art

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With increasingly stringent environmental regulations, the requirements as to the contaminant content of gaseous media, in particular gaseous media to be vented into the atmosphere, further indicated as waste gases, become ever more stringent. Accordingly, processes and apparatus are being developed to reduce the content of objectionable components in waste gases. Such removal 25 can be carried out by adsorption using an adsorbent, by catalytic conversion, or by a combination of these two processes.

Waste gases from which undesired components are removed by using an adsorbent, via catalytic conversion, or by a combination of these processes

include engine exhaust gases, in particular diesel and gasoline engine exhaust gas.

Diesel engines are equipped with an oxidation catalyst to control

5 hydrocarbon, carbon monoxide, and part of the particulate emissions. However, these catalysts only function optimally above a certain temperature, indicated as the "light-off temperature", that is, the temperature above which the catalytic converter converts 50% of the incoming compound. Therefore, in diesel engines the catalyst is often preceded by an adsorbent, which acts to adsorb unburned

10 fuel hydrocarbons at low exhaust gas temperatures, such as during cold start or partial engine load operation, and releases them when the catalyst has reached the higher light-off temperature to effect oxidation.

An additional use of adsorbents in diesel exhaust gas treatment is for

15 NO<sub>x</sub> reduction.

Inherent to the technology, diesel engines are operated at a high air-to-fuel ratio, which leads to relatively high NO<sub>x</sub> formation. Reduction of NO<sub>x</sub> to N<sub>2</sub> requires a temporarily fuel rich operation. WO 96/39244 of Johnson Matthey

20 describes the use of an adsorbent in diesel engines, wherein the adsorbent adsorbs unburned fuel at lower temperature, and releases it at higher temperature. The release of unburned fuel causes a temporary increase in fuel concentration, which leads to increased conversion of NO<sub>x</sub> to N<sub>2</sub>. NO<sub>x</sub> may be converted via NO<sub>x</sub> catalysts and NO<sub>x</sub> trap catalysts.

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Conventional gasoline engines operate in fuel rich mode and the environmentally critical compounds, viz. hydrocarbons, CO, and NO<sub>x</sub> are oxidized and reduced, respectively, by today's standard three-way conversion catalyst systems (TWCs). Nevertheless, also in gasoline engines, cold start

30 emissions can be reduced by in-line adsorbent devices as discussed above.

Additionally, increased attention to fuel economy is leading to the development of fuel-lean gasoline engines, the exhaust characteristics of which are to a certain extent comparable to those of diesel engines, e.g., lower exhaust temperatures and increased NO<sub>x</sub> emissions. With this development, the  
5 adsorbents and catalysts applied for diesel emission reduction will also become attractive for gasoline exhaust applications.

Both in diesel and gasoline engines, when the exhaust temperature is high enough, the hydrocarbons in question will not be adsorbed on the  
10 adsorbent anymore, but pass directly to the catalyst(s). However, the exhaust gases, which by that time may reach temperatures of above 350°C, still encounter the adsorbent. For diesel operation, temperatures of above 350°C, more in particular between 450°C and 650°C, may be reached. For conventional gasoline operation, temperatures above 350°C, in particular of  
15 500°C to 700°C, may be reached. For fuel-lean gasoline engines, the temperature is expected to be lower than for conventional gasoline engines. However, values above 350°C will still be reached.

In the art, zeolites are often used in the treatment of exhaust gases, as  
20 adsorbents or as catalyst components.

The above-discussed WO 96/39244 mentions the use of ZSM-5, ion-exchanged or metal impregnated ZSM-5, silicalite, mordenite, zeolite Y and zeolite P as hydrocarbon adsorber.

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US 5,849,255 describes a catalyst for trapping diesel exhaust hydrocarbons which contains a zeolite with an average pore diameter of greater than about 0.6 nm, a Si/Al ratio over 5, and retention of the crystalline structure at a temperature of 750-850°C in air. Zeolite beta, ultra-stable zeolite Y, and  
30 UTD-1 zeolite are mentioned as examples.

EP 0 499931 describes the use of a zeolite Y with a SAR of 50 in particulate removal from diesel exhaust. US 2002-0114751 describes the use of a zeolite Y with a SAR of 50 loaded with a transition metal for this application.

5 US 2002-0028169 describes the use of a zeolite Y with a SAR of 60 loaded with noble metal for this application.

US 6,407,032 describes a lean NO<sub>x</sub> trap comprising barium nitrate and a zeolite Y.

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EP 0 020 799 and EP 0 003 818 disclose a process for treating exhaust gases from internal combustion engines by converting noxious components using a zeolite Y with a SAR of 4.5-35, preferably 4.5-9, a unit cell size of less than 24.45 Å, and a sorptive capacity for water vapour (25°C, p/p<sub>0</sub> 0.19) of not 15 greater than 12 wt%.

The zeolite used in an adsorbent should be able to adsorb the molecules in question at relatively low temperature, and release them at increasing temperature. Additionally, the adsorbent should be able to withstand the very 20 high temperatures it meets when the engine has reached full operating temperature. As the adsorbent will be used for many years, this latter feature is of particular importance.

As indicated above, zeolites are also used in the catalysts used for 25 treatment of exhaust gases, for example, in NO<sub>x</sub> conversion catalysts or in oxidation catalysts. Zeolites are also used in NO<sub>x</sub> trap catalysts, materials which trap NO<sub>x</sub> under lean fuel conditions and release them under fuel rich conditions for conversion into N<sub>2</sub>. In these applications also, the temperature resistance of the catalyst is of importance for the same reason as given above.

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The object of the present invention is therefore to provide a process for the treatment of waste gas, preferably engine exhaust gas, more preferably diesel or gasoline exhaust gas, wherein the waste gas is contacted with a zeolite Y with exceptional heat stability properties. Preferably, the zeolite  
5 additionally shows good catalytic and adsorbing properties.

#### SUMMARY OF THE INVENTION

In one embodiment, the present invention comprises a process for the  
10 treatment of waste gas wherein the waste gas is contacted with a zeolite Y which has a unit cell size of 24.17-24.45 Å and a water adsorption capacity ( $p/p_0 = 0.2$ ,  $T=25^\circ\text{C}$ ) of at most 5 wt.%, said zeolite Y having a silica-alumina molar ratio of at least 40.

15 In a second embodiment, the present invention comprises a process for the treatment of exhaust gas from a diesel engine, wherein the engine exhaust system is provided with a hydrocarbon adsorbent and/or an oxidation catalyst and/or a  $\text{NO}_x$  conversion catalyst and/or a  $\text{NO}_x$  trap catalyst. The hydrocarbon adsorbent and/or the oxidation catalyst and/or the  $\text{NO}_x$  conversion catalyst  
20 and/or the  $\text{NO}_x$  trap catalyst comprise a zeolite Y which has a unit cell size of 24.17-24.45 Å, a water adsorption capacity ( $p/p_0 = 0.2$ ,  $T=25^\circ\text{C}$ ) of at most 5 wt.% and a silica-alumina molar ratio of at least 40.

Other embodiments of the invention comprise units in which the above  
25 processes may be carried out, zeolite compositions and process conditions.

#### DETAILED DESCRIPTION OF THE INVENTION

The zeolite Y used in the process according to the invention has a unit  
30 cell size of 24.17-24.45 Å, a water adsorption capacity ( $p/p_0 = 0.2$ ,  $T=25^\circ\text{C}$ ) of

at most 5 wt.%, and a bulk silica-alumina molar ratio (also called bulk or chemical SAR) of at least 40. The use of this type of zeolite in this application leads to an adsorbent/converter with high activity in combination with long life.

5        Preferably, the zeolite has a bulk SAR of at least 50, more preferably at least 60, and most preferably at least 70. The bulk SAR will generally be below 200, preferably below 170, more preferably below 140. If the bulk SAR of the zeolite is too low, the adsorption properties of the zeolite will be inadequate, while Y zeolites with a very high bulk SAR and good quality are difficult and  
10      therefore expensive to prepare.

The framework SAR of the zeolite is preferably at least 150, more preferably at least 200.

15       The zeolite Y has a unit cell size of 24.17-24.45 Å. Preferably, the unit cell size is at least 24.18 Å, more preferably at least 24.20 Å, still more preferably at least 24.23 Å, and most preferably at least 24.26 Å. The unit cell size preferably is at most 24.43 Å, more preferably at most 24.36 Å, still more preferably at most 24.33 Å. If the unit cell size is above the specified value, the  
20      selectivity of the zeolite for organic compounds will decrease. The preparation of zeolites with a very low unit cell size and good quality is a costly affair.

The zeolite to be used in the present invention has a water adsorption capacity (WAC) (determined at p/p<sub>0</sub>=0.2 and a temperature of 25°C) of at most  
25      5 wt.%. Preferably, the water adsorption capacity is at most 3 wt.%, more preferably at most 2 wt.%, even more preferably at most 1.5 wt%.

It has been found that there is a strong correlation between the water adsorption capacity, the bulk SAR, and the stability of the zeolite at high

temperatures. Therefore, the water adsorption capacity should be as low as possible, while the bulk SAR is as high as possible.

The WAC is determined as follows. The zeolite is pretreated to dry the  
5 material for 3 hours at 425°C, and then equilibrated at 25°C and a partial water vapour pressure of p/p<sub>0</sub>=0.2.

Another parameter which may be of relevance to the Y zeolites used in the treatment of exhaust gases is the residual butanol test value of the zeolite.  
10 This value, which is determined as described in GB 2,014,970, is a measure for the adsorption of 1-butanol in competition with water, and is a measure for the hydrophobicity of the zeolite. Zeolite powder is activated for 16 hours at 300°C and slurried in a 1-butanol solution in proportions such that the slurry contains one part by weight of 1-butanol, 100 parts by weight of water, and 10 parts by  
15 weight of activated zeolite Y. After gently shaking for 16 hours at 25°C, the supernatant liquid is analysed by gas chromatography. The residual butanol test value (RBT) is defined as the weight percentage of 1-butanol remaining in solution. It has been found that if the zeolite to be used in the present invention has a RBT of below 0.2, in particular below 0.17, more in particular below 0.15,  
20 still more in particular below 0.13, particularly attractive results are obtained.

Zeolites which meet the above requirements are known in the art. They are, e.g., described in US 4,401,566, GB 2,014,970, EP 320, 247, and WO 00/51940.

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As indicated above, zeolites which meet the above requirements show a particularly high thermal stability under the high-temperature conditions which they periodically meet during use. Accordingly, they are particularly suitable for use in the treatment of waste gas according to the invention in processes where  
30 they are periodically subjected to temperatures above 350°C, more in particular

in the treatment of engine exhaust gas, preferably diesel or gasoline exhaust gas, in processes where they are periodically subjected to temperatures above 350°C.

5        The zeolite's high thermal stability under the high-temperature conditions which it periodically meets during use can be seen from the relatively low decrease in micropore volume when the zeolite is subjected to steaming conditions which simulate the fast heating-up and long-term high temperature circumstances in engine exhaust systems.

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The pore volume characteristics are obtained from the nitrogen adsorption isotherm at 78 K, which can be determined using commercially available equipment, e.g., Micromeritics A.S.A.P.-2400 or Gemini-2360. The adsorption  $V_a$  at a relative pressure  $P/P_0$  of 0.30 is interpolated from adjacent points on the adsorption isotherm. To calculate the micropore volume, the nitrogen adsorption isotherm in the range of  $P/P_0 = 0.08$  to 0.80 is converted to a t-plot using the Harkins-Jura equation given by de Boer et al. (J. Colloid Interface Sci. . Vol. 21 (1966), 405), with  $t$  standing for the thickness of the adsorbed layer.

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$$t (\text{\AA}) = \frac{13.99}{0.034 - \log P/P_0}^{\frac{1}{2}}$$

20        Since the t-plots of zeolites are slightly curved, the part of the plot used for determining the slope and the intercept has to be specified. In the present specification the range employed is from  $t$  is 3.5 Å to  $t$  is 5.3 Å. The straight line drawn through the points in this range with the aid of the least squares method has an intercept  $V_{mi}$  and a slope  $\Delta V_a/\Delta t$ . The micro PV is calculated using the formula: micro PV (ml/g) = 0.001547  $V_{mi}$ .

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In one embodiment of the present invention, the zeolite functions as an adsorbent which adsorbs undesired compounds, in particular organic compounds, from waste gas at low temperature, e.g., below 120°C, and desorbs them at a higher temperature, e.g., above 120°C.

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This goes in particular for adsorption of undesired components from engine exhaust gases, such as unburned fuel components. For diesel exhaust, the adsorption preferably takes place at a temperature below 120°C, while the desorption takes place at a temperature above 120°C. For conventional 10 gasoline exhaust, the adsorption preferably takes place at a temperature below 170°C, while the desorption takes place at a temperature above 170°C. For lean fuel gasoline exhaust, the adsorption preferably takes place at a temperature below 120°C, while the desorption takes place at a temperature above 120°C.

15 In diesel exhaust, the desorbed hydrocarbons are led to an oxidation catalyst, to a NO<sub>x</sub> conversion catalyst, or to a NO<sub>x</sub> trap catalyst. In conventional gasoline exhaust, they are led to a TWC catalyst system. In lean-burn gasoline systems gases can be converted by a NO<sub>x</sub> conversion catalyst or captured in a NO<sub>x</sub> trap instead of TWC's. The above-mentioned zeolite can also be used in 20 said oxidation catalysts, NO<sub>x</sub> conversion catalysts, and NO<sub>x</sub> trap catalysts.

For use as oxidation catalyst, the zeolite is preferably provided with noble metals such as platinum, palladium, or rhodium.

25 For use in a lean NO<sub>x</sub> catalyst, the zeolite is preferably provided with a noble metal of Group VIII of the periodic table of elements and/or with a non-noble metal of Group VIII of the periodic table of elements and/or with a metal of Group I. Noble Group VIII metals include platinum and palladium. Non-noble metals of Group VIII include nickel, cobalt, and iron. Copper is the most suitable 30 metal of Group I.

For use in a NO<sub>x</sub> trap, the zeolite is preferably provided with an alkaline earth metal such as calcium, barium, or strontium. In this technology, NO<sub>x</sub> is first oxidised to NO<sub>2</sub> by catalytic metals useful for such oxidation, e.g., precious metals such as platinum, palladium, and rhodium. The NO<sub>2</sub> is then trapped on the surface of the catalyst in the form of a nitrate. The system is periodically operated under fuel rich conditions, which effect release of the NO<sub>x</sub> and conversion thereof into N<sub>2</sub>.

These catalysts are therefore preferably provided with noble metals as specified above, and a compound suitable to trap the nitrate, e.g., barium carbonate.

A combination of adsorption and catalytic conversion is also envisaged for the present invention. The present invention therefore also pertains to the use of a combination of an adsorbent and a catalyst in the treatment of waste gas, preferably engine exhaust gas, more preferably diesel or gasoline engine exhaust gas, wherein at least one of the adsorbent and the catalyst comprises the above-described zeolite. Accordingly, the present invention also pertains to a process for the treatment of exhaust gas from a diesel engine, wherein the engine exhaust system is provided with a hydrocarbon adsorbent and/or an oxidation catalyst and/or a NO<sub>x</sub> conversion catalyst, and/or a NO<sub>x</sub> trap catalyst, wherein the hydrocarbon adsorbent and/or the NO<sub>x</sub> conversion catalyst, and/or the NO<sub>x</sub> trap catalyst comprise a zeolite Y with the above properties. The present invention further pertains to a process for the treatment of exhaust gas from a gasoline engine, wherein the engine is provided with a hydrocarbon adsorbent and a TWC catalyst or NO<sub>x</sub> conversion catalyst and/or a NO<sub>x</sub> trap catalyst, wherein the hydrocarbon adsorbent and/or the NO<sub>x</sub> conversion catalyst, and/or the NO<sub>x</sub> trap catalyst comprise a zeolite Y with the above properties.

The zeolite is preferably used in the treatment of exhaust gases in the form of a thin layer on a monolithic carrier. Monolithic carriers are known in the art and include, e.g., the well-known honey-combs. The zeolite is applied onto 5 the carrier in manners known in the art, e.g., by contacting the carrier with a slurry of the zeolite, followed by drying and calcining. This process is often indicated as preparing a wash-coat.

Accordingly, the present invention also pertains to a unit suitable for the 10 treatment of exhaust gas as described above, which comprises a zeolite with the above-mentioned properties.

The unit preferably is a monolith at least part of the surface of which is coated with the zeolite. Optionally, the monolith can comprise one or more of 15 the metal components indicated above.

#### EXAMPLE

The hydrothermal stability of zeolites Y1 to Y4 was determined by 20 steaming the zeolites for 5 hours at 850°C under a flow of air containing 10 vol% H<sub>2</sub>O.

The relative crystallinity was determined by taking the crystallinity of the zeolite after steaming relative to the crystallinity before steaming. The 25 crystallinity of the zeolite was determined by measuring the XRD peak surfaces relative to an internal zeolite Y standard.

The relative crystallinity after steaming was taken as a measure for the hydrothermal stability: the higher the relative crystallinity, the higher the 30 hydrothermal stability.

The relative crystallinity of the different zeolites is shown in Table I.

Zeolites Y1, Y2, and Y3, having a SAR in the range 4.5-35, a unit cell size of less than 24.45 Å, and a WAC of not greater than 12 wt%, are representative for the zeolites of EP 0 020 733 and EP 0 003 818.

Zeolite Y4 is a zeolite according to the present invention.

As can be seen from Table I, the zeolite according to the present invention has a higher heat stability than the zeolites representative for EP 0 020 733 and EP 0 003 818.

Table I

Zeolite	Unit cell size (Å)	WAC ( $p/p_0=0.2$ , $T=25^\circ\text{C}$ )	Bulk SAR	Relative crystallinity (%)
Y1	24.35	5.7	12	89
Y2	24.33	4.6	16	91
Y3	24.31	1.9	29	94
Y4	24.29	1.3	56	99